



Review

A review of blended cathode materials for use in Li-ion batteries

Satishkumar B. Chikkannanavar^{a,*}, Dawn M. Bernardi^a, Lingyun Liu^b^a Ford Motor Company, Cell Integration and Test Section, Advanced Electrification Center, 2400 Village Rd, Dearborn, MI 48124, USA^b Ford Motor Company, Energy Storage Research, Research and Advanced Engineering, 2101 Village Rd, Dearborn, MI 48121, USA

HIGHLIGHTS

- This review surveys the up to date literature advances.
- Unique advantages of blended materials are listed.
- Challenges to existing materials and future directions are covered.
- Review provides important status update of the blended materials.

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ABSTRACT

Several commercial automotive battery suppliers have developed lithium ion cells which use cathodes that consist of a mixture of two different active materials. This approach is intended to take advantage of the unique properties of each material and optimize the performance of the battery with respect to the automotive operating requirements. Certain cathode materials have high coulombic capacity and good cycling characteristics, but are costly and exhibit poor thermal stability (e.g., $\text{LiNi}_x\text{Co}_{1-x-y}\text{Al}_y\text{O}_2$). Alternatively, other cathode materials exhibit good thermal stability, high voltage and high rate capability, but have low capacity (e.g., LiMn_2O_4). By blending two cathode materials the shortcomings of the parent materials could be minimized and the resultant blend can be tailored to have a higher energy or power density coupled with enhanced stability and lower cost. In this review, we survey the developing field of blended cathode materials from a new perspective. Targeting a range of cathode materials, we survey the advances in the field in the current review. Limitations, such as capacity decay due to metal dissolution are also discussed, as well as how the appropriate balance of characteristics of the blended materials can be optimized for hybrid- and electric-vehicle applications.

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1. Introduction

1.1. Motivations for blending cathode materials

There is an intense interest in the battery industry to identify ways to improve the cathodes¹ used in Li-ion batteries for automotive-propulsion applications in terms of energy, power, safety, life, and cost. Blending cathode materials [1–11] is a new approach to designing better batteries for hybrid electric, plug-in hybrid electric, and battery electric vehicles (HEVs, PHEVs, and BEVs, respectively). The active material for a 'blended' cathode is comprised of a physical mixture of two or more distinct lithium

intercalation compounds.² The motivation for blending these compounds is to achieve a more balanced performance compared to what is possible with any individual compound. For example, in a blended cathode system composed of LiMn_2O_4 (LMO, also referred to as "spinel"³) and $\text{LiNi}_x\text{Co}_{1-x-y}\text{Al}_y\text{O}_2$ (NCA), the NCA has a higher capacity ($\sim 195 \text{ mAh g}^{-1}$) and is more chemically stable (i.e., life); but its thermal stability is inferior. Alternatively, spinel has a higher operating voltage and better rate capability and is less costly. Because many of the shortcomings of spinel are favorable attributes of NCA, blending these two materials has received considerable attention [2]. Although the NCA/spinel blend may have less desirable storage life than pure NCA, the cost, energy, power and safety

* Corresponding author.

E-mail address: satishbc@gmail.com (S.B. Chikkannanavar).

¹ In this review we use the term "cathode" to refer to the positive electrode and anode refers to the negative electrode, although in rechargeable batteries the positive electrode is an anode on charge.

² In the scanning electron micrograph shown in Fig. 2(a) (Ref. [2]), the two distinct materials of which this blended cathode is fabricated can be readily discerned.

³ Although the term "spinel" generally refers to a type of chemical structure, we use the term to refer to the lithium–manganese-oxide spinel compound $\text{Li}_x\text{Mn}_2\text{O}_4$.

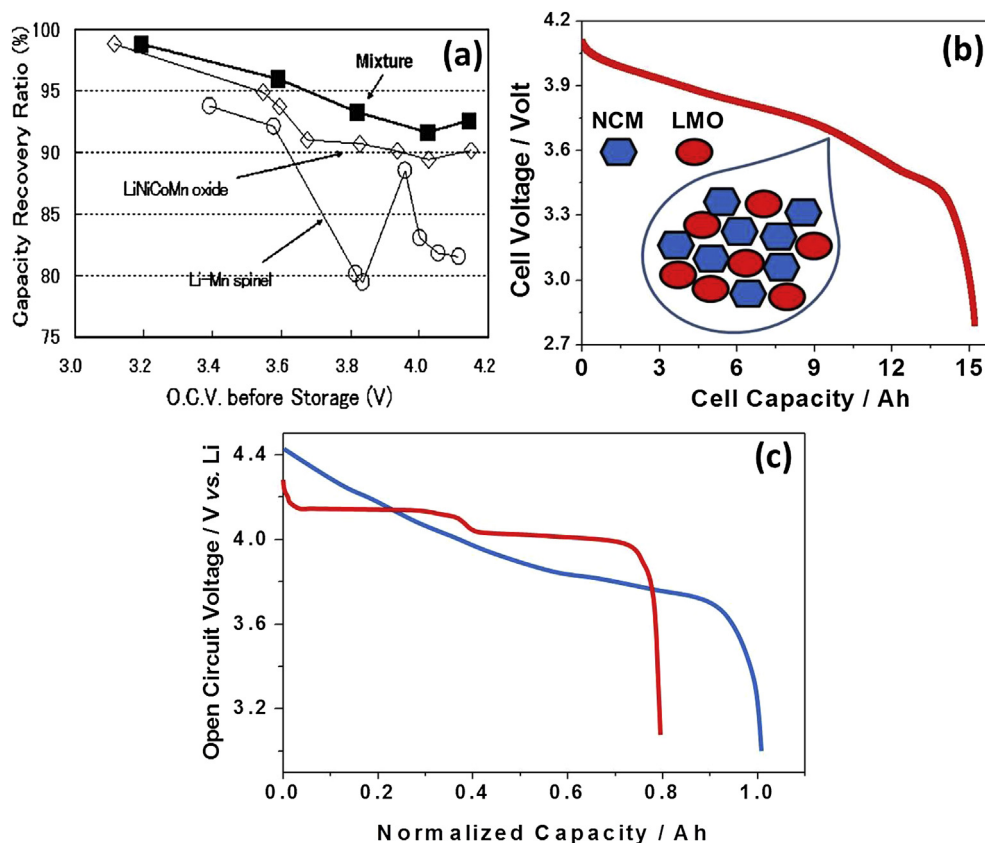


Fig. 1. (a) Capacity recovery ratio for the parent compounds spinel and NMC and their blend (40 wt% spinel) after storage for 30 days at 45 °C in 18650 cells (from Kitao et al. [1]), (b) voltage vs. capacity profile during 1C discharge for a commercial pouch cell made of a NCM/LMO blend and (c) open-circuit voltage vs. capacity (normalized) profiles for NCM and LMO in half cells [13,23].

advantages attributable to spinel may outweigh the life issues for certain applications. Although blending may be useful for optimizing performance with respect to several attributes, there may be other characteristics of the blended system that are not improved by this approach and each cathode must be carefully considered with respect to its application. Thus, blending allows the parent cathode materials to complement each other; that is, a weakness of one material alone is strengthened in the blend. The primary purpose of this communication is to survey the state-of-the-art of blended cathode materials for use in Li-ion batteries.

High-rate cycling capability to meet the power and energy requirements of hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and battery electric vehicles (BEVs) is another important characteristic for blended cathode materials to possess. In these applications, mitigation approaches such as surface treatment may be necessary to counter the loss of capacity due to shrinking and swelling of active-material particles during cycling [9,11]. Furthermore, limitations such as metal dissolution from the host metal oxide, which affects the performance of certain blended cathode materials, need to be addressed. The enhanced storage life for a cell made with a blend of $\text{LiNi}_{0.4}\text{Mn}_{0.3}\text{Co}_{0.3}\text{O}_2$ and LMO relative to a cell made with LMO alone as reported in early studies of Kitao et al. [1] is shown in Fig. 1(a). The researchers examined capacity retention during storage at 45 °C in 18650 cells and found that capacity retention was improved over spinel-only cathodes for a 40% spinel blend. To our knowledge, these results are the only example of improved cell storage life in a blended system with spinel as the parent material. In a blended cathode system, the Li insertion/extraction in one parent cathode material may be

influenced by the other. Also, Li diffusion and other material characteristics influence the charge/discharge profile of the blended system. In fact, one of the major outcomes of a blended cathode system is the modification of the voltage (or state-of-charge, SOC) profile relative to that of parent cathode materials. Fig. 1(b) shows typical example of a voltage vs. capacity profile for a commercial pouch cell which is made with a blended cathode consisting of NMC and LMO and a graphitic anode (obtained in our laboratory). The “Ford Focus” BEV and “Chevrolet Volt” utilize pouch cell batteries fabricated using a blend of NMC and spinel. Discharge profiles for two cathodes in half cells are shown together in Fig. 1(c). The thermodynamic open circuit voltage (OCV) behavior of the blend reflects the equalized lithium activities of the individual parent compounds [2]. Several publications [1–3,6,8], account for the complex behavior associated with Li insertion/extraction dynamics in blended systems. Each parent cathode material in a blended system influences the cell SOC and Li diffusion characteristics and contributes to coulombic capacity during cycling. Due to these novel aspects, blended cathode materials are presently an active area of study. Researchers have explored parent cathode materials for blends based on layered oxides, such as $\text{LiNi}_x\text{Mn}_{1-x}\text{Co}_{1-2x}\text{O}_2$ (NMC) [1], NCA [2], LiCoO_2 (LCO) [4,7,9], $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ [3], and $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M} = \text{Mn, Co, Ni}$)⁴ [10,11], as well as spinel [5,6,8] and LiFePO_4 (LFP) [10]. In addition to the blended materials, which are physical mixtures, we will also discuss the Li_2MnO_3 -stabilized compounds (e.g.,

⁴ Also referred to as Li_2MnO_3 -stabilized layered oxides or Li-rich complexes.

Table 1Summary of parent cathode materials and blends* with their respective capacity, cell voltage and energy density ([†]cycle life is being targeted at present).

Parent cathode materials & blends*	Capacity mAh g ⁻¹	Avg. voltage (V vs Li/Li ⁺)	Energy density	
			Wh kg ⁻¹	Wh L ⁻¹
LiCoO ₂ [14]	151	4.00	602	3073
LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂ (NCA) [14]	195	3.80	742	3784
LiMn ₂ O ₄ (spinel) [14]	119	4.05	480	2065
LiNi _{1/3} Mn _{1/3} Co _{1/3} O ₂ (NMC 333) [14]	153	3.85	588	2912
LiMn _x Co _y Ni _z O ₂ (NMC non-stoichiometric) [14]	220	4.0	720	3600
LiFePO ₄ (iron phosphate) [14]	161	3.40	549	1976
xLi ₂ MnO ₃ ·(1-x)LiMO ₂ [12]	250–280	~4.0	–	–
*LiCoO ₂ – LiNi _{1/3} Mn _{1/3} Co _{1/3} O ₂ (7:3) [9]	180	~3.9	–	–
*xLi ₂ MnO ₃ ·(1-x)LiMO ₂ – LiFePO ₄ [10]	220	~3.6	>890	–
*Li[Li _{0.2} Mn _{0.54} Ni _{0.13} Co _{0.13}]O ₂ –LiV ₃ O ₈ [3]	275	3.0–4.0	–	–
*Li[Li _{0.2} Mn _{0.54} Ni _{0.13} Co _{0.13}]O ₂ –Li ₄ Mn ₅ O ₁₂ [3]	250	3.0–4.0	–	–
*Li[Li _{0.17} Mn _{0.58} Ni _{0.25}]O ₂ –LiFePO ₄ [33]	~200	3.0–4.0	>700	–
Sulfur (in Li–sulfur system) [16]	~1000 [†]	2.0–2.4	1550	–

Li_{1.05}(Mn_{1/3}Ni_{1/3}Co_{1/3})_{0.95}O₂) recently developed by Thackeray and coworkers [12,13].

1.2. Parent cathode material characteristics

Before we proceed with a discussion of the blended materials, it is useful to compare the different parent cathode materials individually. The capacity, voltage and energy density of common cathode materials for Li-ion batteries are listed in Table 1. Also listed are respective values for certain blended cathode materials based on literature and related sources. For a review on various cathode materials and the challenges involved in their design for high coulombic capacity, we refer the reader to Refs. [15–17]. Note that the layered oxides (e.g., NMC, NCA, xLi₂MnO₃·(1-x)LiMO₂ (where M: Mn, Ni, Co)) possess relatively high capacity and energy density. Cathode materials with the composition xLi₂MnO₃·(1-x)LiMO₂ are also referred to as Li₂MnO₃-stabilized layered oxides or Li-rich complexes. Besides these materials, sulfur-based cathode materials are promising in terms of high energy density [18]; however, further work is in progress to improve cycling and life characteristics. In the following sections we will discuss various blended cathode materials composed of these parent materials and the associated properties of the blended materials.

2. Performance characteristics and properties of blended cathodes

2.1. Blends of spinel and layered oxides (LCO, NCA, NMC)

Relative to LCO, NCA and NMC, spinel is lower in cost, more environmentally benign and possesses a higher operating voltage, higher rate capability [19,20], and better thermal stability [21,22]. These characteristics make spinel an attractive material for blending with layered oxides that have a higher coulombic capacity, but higher cost, lower thermal stability and lower rate capability. Spinel has a lower coulombic capacity [19] and the disadvantages such as crystal-structure transformations during cycling, oxygen deficiency, Mn dissolution etc. [23–30] can lead to a higher capacity-fade than observed in the layered oxides. Several groups have reported results for the spinel/layered-oxide blended cathode systems [1,2,8]. Albertus et al. [2] examined a spinel–NCA (1:1 wt%) blend (Fig. 2) and compared voltage profiles for the parent materials to blend at various rates along with theoretical simulations. They found that the blended cathode material has a higher average voltage at high rates (e.g., 5C) than NCA alone and superior overall rate performance [2]. Similar studies on spinel–NCA blends by Tran et al. [8] (Fig. 3) showed the same advantage of

the blend over the parent materials. Their results showed that a blended cathode material made of 33.3% NCA showed the best discharge behavior at the 5C rate relative to other possible mixtures (Fig. 3(a)) [8]. Investigations of the SOC behavior of the 1:1 spinel/NCA blend and the parent cathode materials indicated that the spinel and NCA phases charge independent of each other (see Fig. 3(b)) [8]. For the 1:1 blend, NCA was found to charge (i.e., contribute to cell capacity) before spinel; spinel would follow and act as the primary contributor to cell capacity during Li extraction. In addition, the blend showed improved thermal stability relative to the layered oxide [8].

Liu et al. [24] investigated blends made of NMC and spinel in different ratios and demonstrated that a 50:50 (wt%) spinel–NMC blend exhibited lower decay in capacity than other combinations. The authors also investigated the crystallographic response of spinel–NMC blends (1:1 wt%) and single-compound cathode materials (in half cells) during the charge/discharge process using X-ray diffraction (XRD). Fig. 4(a) illustrates XRD patterns of the NMC electrodes when charged from 3.0 V to 4.5 V vs. Li/Li⁺. Peak shifts are observed within the OCV window of 3.0 V–4.0 V vs. Li/Li⁺ and remain unchanged for voltages greater than 4.0 V vs. Li/Li⁺. The Bragg peaks for spinel (see Fig. 4(b)) start to shift to higher angles when the voltage reaches 4.0 V vs. Li/Li⁺. The XRD patterns of the NMC–spinel composite cathode are plotted in Fig. 4(c). The crystal structure changes of the composite electrode follow the similar trend of the individual materials. The indices H and C are used to denote the hexagonal phase of NMC and the cubic phase of spinel, respectively. For the blend, equilibrium lithium extraction takes place only in the layered compound (NMC) when the cell OCV is lower than 4.0 V vs. Li/Li⁺. When the cell OCV reaches 4.0 V vs. Li/Li⁺, the spinel phase plays the major role in lithium extraction. This behavior would be in accordance with the thermodynamic OCV behavior of the blend, which can be constructed from OCV vs. degree of lithiation data versus a common reference electrode (RE) for the parent compounds by mapping blend OCV against the “mixing cup” degree of lithiation of the blend obtained from a lithium material balance [2]. The higher voltage vs. RE of spinel (relative to that of NMC) would render the NMC nearly dormant with respect to lithium uptake from a fully de-lithiated state of the blend down to a certain degree of lithiation of the blend (and associated blend OCV), depending upon the blend ratio. The results of Liu et al. [24] indicate that the blend OCV associated with this certain degree of lithiation for the 50:50 (wt%) spinel–NMC blend is approximately 4 V vs. Li/Li⁺. Then from this certain degree of lithiation of the blend, with the spinel approaching the full lithiation, the NMC will be the more prominent acceptor of lithium as the blend then reaches full lithiation. From these arguments we see that it is possible

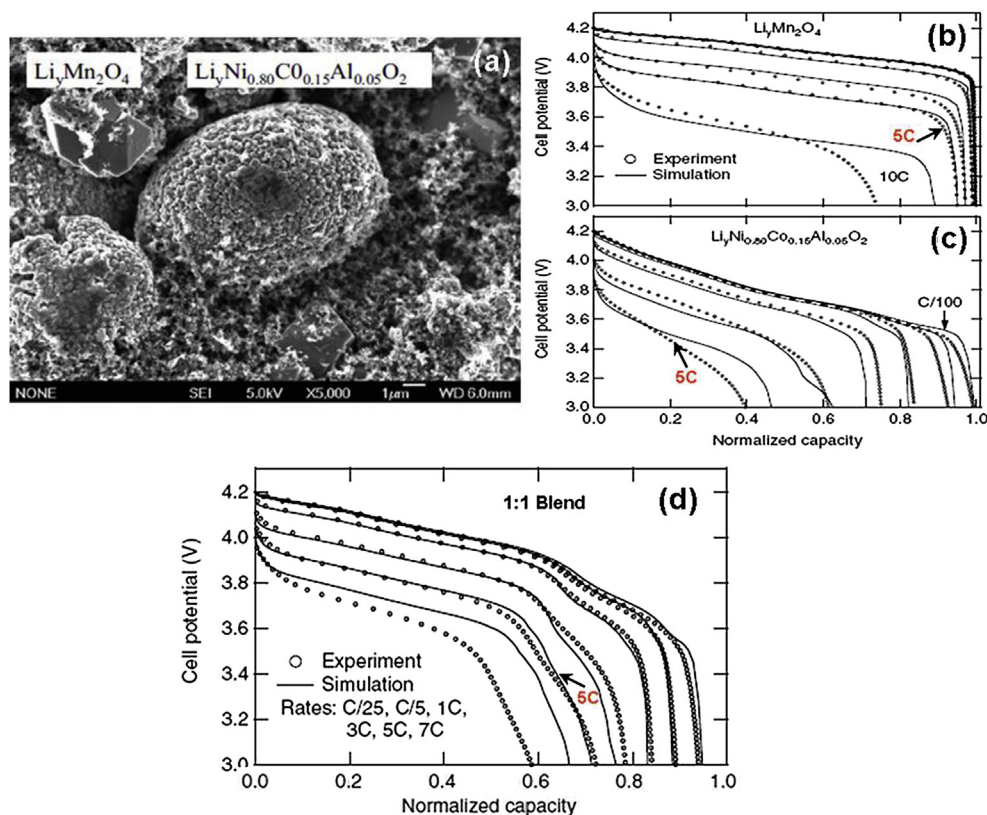


Fig. 2. (a) Scanning electron micrograph of a blended spinel–NCA material, wherein, parent cathode material particles are seen together in the mixture. Rate performance experiments and simulations of a cathode composed of (b) pure LiMn_2O_4 at the rates of C/25, C/5, 1C, 3C, 5C, and 10C, (c) pure $\text{Li}_y\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ at the rates of C/100, C/25, C/5, 1C, 3C, and 5C. (d) Rate performance of the 1:1 blend (wt%) at C/25, C/5, 1C, 3C, 5C, 7C rates (from Albertus et al. [2]).

that cycle-life studies restricted to a cell SOC window associated with the positive electrode voltages being greater than 4 V vs. Li/Li^+ would result in a larger performance degradation than for cells with pure spinel. That is, the blend could allow for a larger range of spinel lithiation to be utilized than in the pure material for the same coulombic throughput and result in more degradation. In this case the purpose of blending spinel with NMC would be defeated; battery life is a weakness for spinel, which would be further weakened

in the blend, rather than strengthened. Our arguments also suggest that in the best case, the high-voltage component in a blend should be the most resilient in terms of storage and cycle life. Chemically speaking, the pairing of high-voltage operation and greater resistance to storage and cycle decay may be difficult to achieve, since high voltages are likely to enable more degradation pathways. In the spinel–NMC blend the life attributes come from the low-voltage component, NMC.

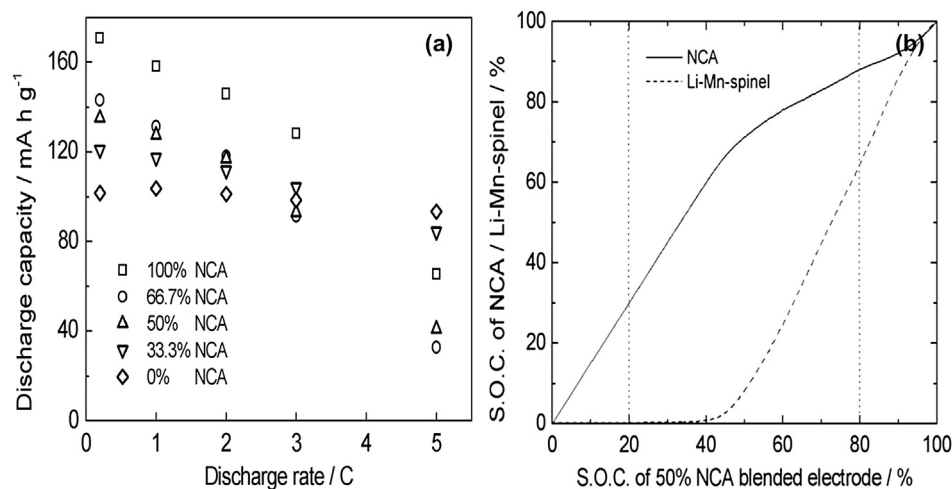


Fig. 3. (a) Rate performance of blended electrodes (spinel–NCA) with different compositions in a LiPF_6 electrolyte at different charge/discharge rates between C/5 and 5C; cycling potential range 3.0–4.3 V (cells with graphite negative electrode). (b) Dependency of the SOC of NCA and LiMn_2O_4 on the SOC of the blend. The composition of the blend was: 50 wt % NCA–50 wt % LiMn_2O_4 spinel (from Tran et al. [8]).

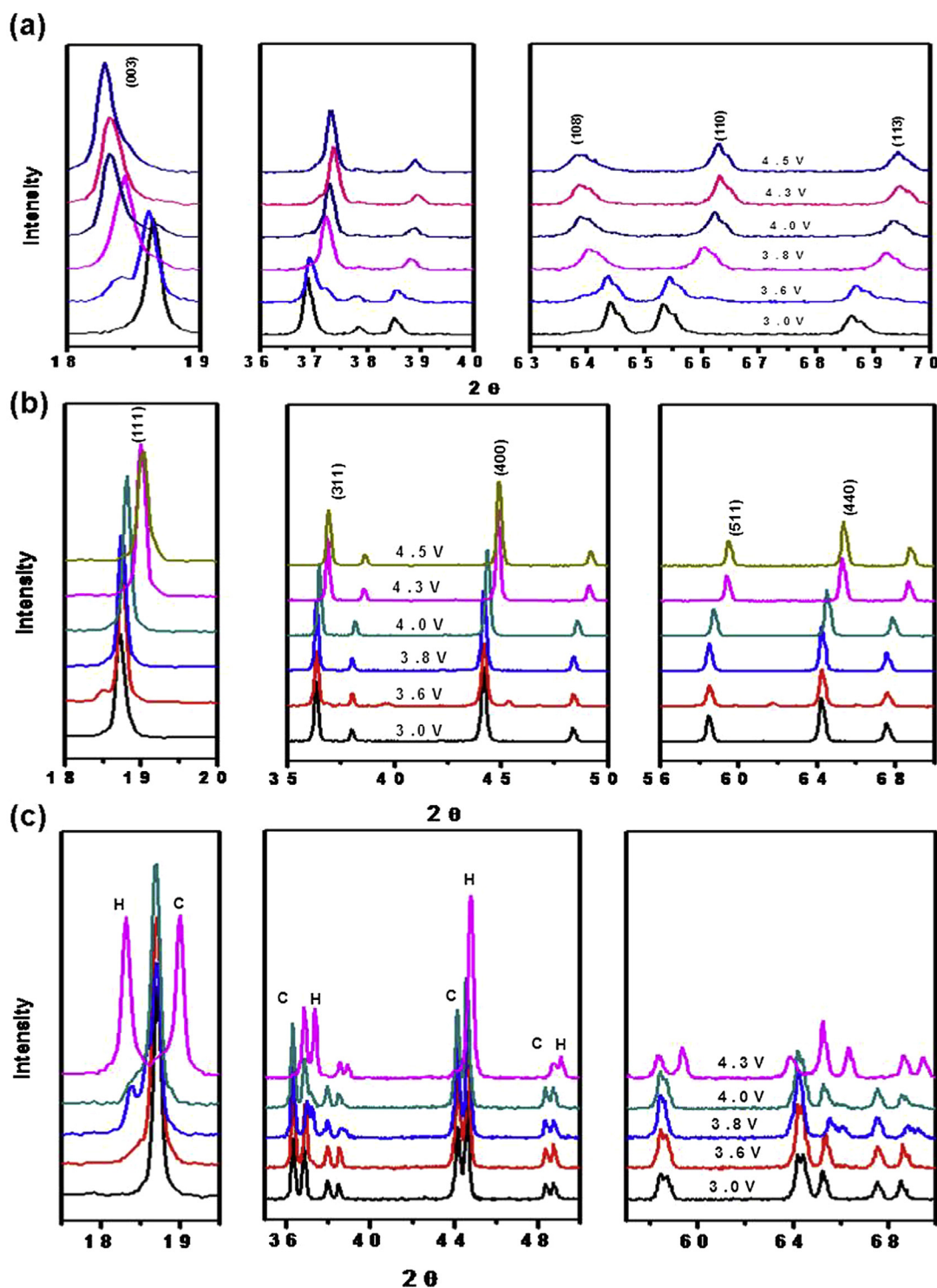


Fig. 4. XRD patterns of (a) NMC electrode, (b) spinel electrode and (c) NMC–spinel blended (1:1 wt%) electrode (in half cell) charged to different voltages. Note the shift of peaks to higher angle during charge cycle. C and H refer to cubic and hexagonal structure of spinel and NMC, respectively (from Liu et al. [24]).

A maximum in capacity loss of spinel at a certain degree of lithiation in storage tests [35] is another aspect relating to the problem of Mn dissolution from this material (see also Fig. 1(a)). Doi et al. [35] observed maximal capacity decay at an OCV of approximately 3.99 V vs. Li/Li^+ (i.e. at 75% depth of discharge (DOD)), as shown in Fig. 5. This OCV corresponds to a degree of lithiation of about 0.78 and would be associated with a certain cell-design dependent SOC. Also, capacity degradation during cycling at high

voltage has been attributed to oxygen deficiency and electrolyte stability, as discussed earlier [20,23–30]. Here again, spinel structure transformations and associated effects play a crucial role. It follows that a cell would exhibit maximal capacity loss in storage-life testing at this particular SOC, which would also be dependent on blend ratio. Decreasing the ratio of spinel to NMC will allow the 3.99 V vs. Li/Li^+ to occur at a more highly de-lithiated state of the blend, which would correspond to a higher cell SOC.

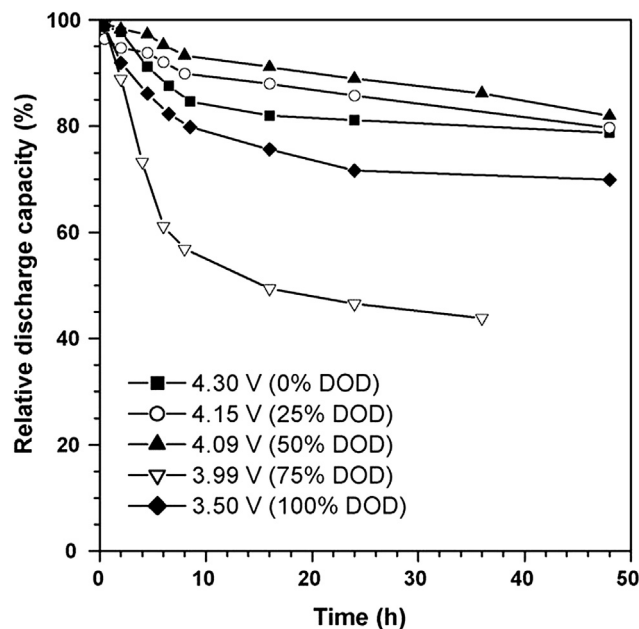


Fig. 5. Variation of relative discharge capacities of LiMn_2O_4 thin films with time of storage at 0%, 25%, 50%, 75%, and 100% DOD in $1 \text{ mol dm}^{-3} \text{ LiPF}_6/\text{Propylene Carbonate}$ at 80°C (from Doi et al., [35]).

The life of Li-ion batteries can also be affected by crystal-structure transformations (i.e., unit-cell lattice constant changes) in the cathode materials, which in turn result in volume changes during Li extraction/insertion cycles. Nam et al. [6] investigated blended cathode materials made of spinel and NMC and observed these structural changes during charge/discharge cycling in Li half cells and pouch cells with a graphitic negative electrode. During charge, both spinel and NMC exhibited contraction of their cubic and hexagonal cells, respectively. Although volume changes ($\sim 5\%$ for spinel and $<1\%$ for NMC) were observed for both the parent cathode materials (in half cells), NMC contributed substantially to the capacity during initial charging. This was followed by a large contribution to the capacity from spinel, with associated volume reduction in the Li half cells (see Fig. 6(a)). The overall change in molar volume is isotropic for spinel, while it is anisotropic for the layered NMC. For the Al pouch cells, the authors observed a lower change in unit-cell volume for NMC relative to spinel, as shown in Fig. 6(b).

It is well known that spinel exhibits relatively high capacity decay, especially at elevated temperature (above 50°C) and that this decay is attributed to Mn dissolution [25]. Cell capacity decay can also be attributed to structural changes (e.g., Jahn-Teller distortion) [26–30] during cycling which can lead to loss of oxygen, Mn disproportionation (i.e., $2\text{LiMn}_2\text{O}_4 \rightarrow \text{Li}_2\text{O} + 3\text{MnO}_2 + \text{MnO}$), particle cracking and loss of particle contact [23,25–34]. Lithium-ion batteries employing spinel as a cathode material may therefore be particularly challenged in automotive propulsion applications where long battery life over a wide range of operating temperatures is essential. Manganese dissolution from spinel is accelerated by HF, which is generated by side reactions during battery operation (e.g., $\text{LiPF}_6 + 4\text{H}_2\text{O} \rightarrow 5\text{HF} + \text{LiF} + \text{H}_3\text{PO}_4$) [25]. During the discharge process, lithium accumulation at the surface of spinel particles leads to Mn^{3+} rich composition (at $\sim 4 \text{ V}$ vs. Li/Li^+) [26–30], which in turn leads to transformation of the cubic phase into a tetragonal phase. The associated lattice-parameter change and misfit in phases leads to dissociation of the tetragonal phase from the spinel bulk

particles. This often leads to cracks in the spinel particles during cycling [31], further resulting in a loss of electrochemically active particle volume and thus loss in capacity. Also, free energy calculations for the Mn-ion dissolution reaction indicate that the reaction is endothermic in the absence of HF, while it is exothermic⁵ in its presence due to the high reactivity of fluorine ions [34]. The dissolution of Mn from MnO_2 and MnO has also been shown to be accelerated in the presence of HF [34]. Another effect that is associated with Mn dissolution and influences battery performance is that the dissolved Mn ions migrate to the negative electrode and deposit as a surface layer following reduction (see reaction scheme below).



A deposited layer of Mn on the negative electrode could thwart the transport of lithium during charge/discharge cycling, which in turn could affect cell cycle life.

From early years, Numata et al., [36] suggested blending of spinel with a layered cathode material (e.g., $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$) in order to inhibit Mn dissolution. Recent aging studies of spinel–NCA cathode materials [8] indicated that Mn was dissolved from the cathode materials due to reaction with HF (discussed above). For these blended cathodes stored in electrolyte, the dissolved Mn was $\sim 33 \text{ ppm}$, whereas for a cathode made of 1:1 (wt%) spinel–NCA, the Mn content was reduced to $<1 \text{ ppm}$ [8]. Besides spinel, other Mn-containing cathode materials (e.g., NMC) are also susceptible to metal dissolution. Aging studies of NMC particles in the carbonate solvents indicate that besides Mn, Co and Ni are also prone to dissolution due to the HF reaction [37]. Thus one will also see dissolved Co and Ni along with Mn in cells employing spinel/NCM blends.

Clearly, lithium-ion batteries employing spinel as a cathode material are challenged in applications in which cell life is of particular importance. Although the strengths of spinel as a parent compound relative to most others are safety, cost, and voltage, there are other means of addressing these factors. Safety concerns can be addressed at the system level in many applications. Not only should warranty costs be considered, but there are other means of reducing cell cost than through the cathode materials (e.g. electrolyte solution). Also, when spinel is used as a parent material to increase voltage, the preferential lithium insertion/extraction of spinel over most of the cell SOC range (see above discussion) may not be advantageous.

2.2. Blends of olivines (LiFePO_4 , LiMnPO_4) and layered oxides (LCO, NMC)

Olivine-structured cathode materials, such as LiFePO_4 and LiMnPO_4 , possess better thermal stability characteristics than layered oxides [38]; however, these olivines possess lower voltage (i.e., 3.4 V vs. Li/Li^+) and a relatively long, flat voltage plateau during charge/discharge cycles (see Fig. 7(a)), which renders them less attractive for HEV, PHEV, and BEV applications. In these applications a flat voltage profile makes it difficult to distinguish the changes in SOC. One approach to overcome this limitation is to blend LiFePO_4 with layered oxides such as LCO or NMC. Whitacre et al., [39] demonstrated advantages in cost, safety, and high-rate characteristics for blends of LiFePO_4 with $\text{Li}[\text{Li}_{0.17}\text{Mn}_{0.58}\text{Ni}_{0.25}]\text{O}_2$. Gallagher et al. [10] investigated a blend made with the high-capacity layered oxide, $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ and LiFePO_4 . The cell voltage profile from the blended cathode material is shown in

⁵ Fluorine ions increase the reaction energy.

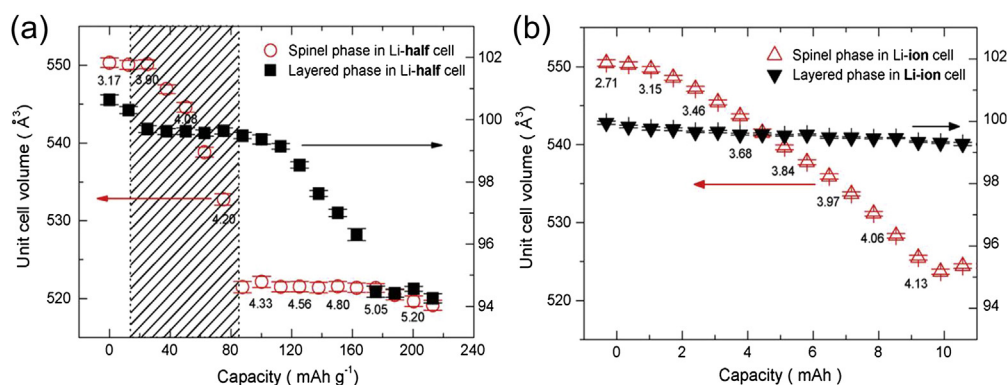


Fig. 6. Variations of unit cell volumes of a $\text{LiMn}_2\text{O}_4/\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ blended cathode in (a) the Li half cell and (b) pouch-type Li-ion cell during charge (numbers marked on the graphs correspond to the cell voltages) (from Nam et al. [6]).

Fig. 7(b). As described above, continuous variation of voltage or SOC (see Fig. 7(b)) aids in the monitoring of cell SOC and blending can lead to improved power capability and thermal stability. This approach is an attractive possibility for use in PHEV-related applications [10].

Blends of LiFePO_4 with $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ have also been studied by Zheng et al. [40]. However, these cathode materials have lower capacity and their voltage profiles consist of multiple plateaus due to the various oxidation states of vanadium. In another approach, coating the particles of a parent cathode material with another cathode material produced the performance characteristics similar to blending the two materials. This helps to overcome the irreversible capacity loss associated with the parent cathode material. Coating $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})\text{O}_2$ with LiFePO_4 [41] has been shown to reduce irreversible capacity decay in a high capacity ($\sim 163 \text{ mAh g}^{-1}$) formulation. Other investigators have suggested that coating active material particles with an ionic conductor provides enhanced capacity retention and long life [41].

2.3. Blends of LiCoO_2 with NMC, NCA or spinel

LiCoO_2 , the most commercially used cathode material, is used in applications such as laptop computers, cell phones and other portable electronic devices. The disadvantage of LCO is that it possesses relatively poor thermal stability, especially during overcharge. In the de-lithiated state, LCO is particularly unstable and thermal runaway events can occur [21,22]. In order to address this thermal instability, researchers have focused on blending LCO with other cathode materials such as LFP, spinel or other layered oxides

[4,7,9]. Generally, the blending improves thermal stability for a given amount of coulombically active material to the extent that would be expected by the reduced amount of LCO. Several research groups have also explored coating approaches where ionically conductive materials (e.g., AlF_3 etc.) are used for coating the active material particles [9,11]. Such coatings facilitate ion transport through particle surfaces, help to retain particle integrity during long term cycling, and enhance thermal stability. An example of improvement in thermal stability for LCO and NMC along with their blend for uncoated and coated conditions is illustrated in Fig. 8 [9]. During overcharge conditions, LCO forms oxides of cobalt which are unstable to reaction with solvents and can initiate a thermal runaway [21,22]. Both the uncoated and coated LCO show inferior thermal stability relative to the blended materials (see Fig. 8). The authors of this study propose that surface coatings protect active material particles from oxidation and dissolution effects induced by reaction products of electrolyte solvents and salt. Li et al. [42] investigated the effect of coating of FePO_4 on NMC particles and found that the coating stabilized the structure during long term cycling and it also helped to inhibit charge-transfer resistance increase during cycling. In a unique approach to address thermal-runaway conditions of LCO, Imachi et al. [43] proposed a layered LCO/LFP structure, in which the phosphate layer acts as a resistive barrier to limit the flow of current. This composite cathode structure has been shown to inhibit overheating effects during overcharge conditions.

In order to reduce cost, many researchers have explored using Ni and Mn doping in place of Co in LiCoO_2 . Cyclic voltammetry studies by Ma et al. [44] examined charging behavior of blended

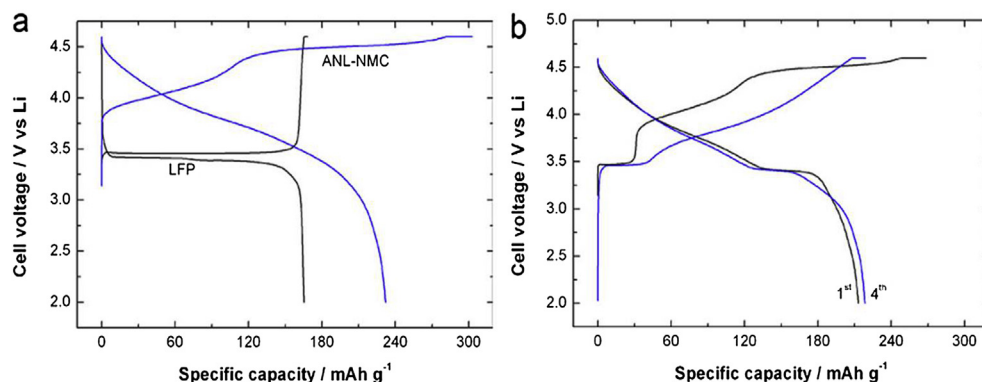


Fig. 7. Charge–discharge data for (a) unblended $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.44}\text{Mn}_{0.31}\text{Co}_{0.25}\text{O}_2$ (ANL-NMC) and LiFePO_4 (LFP) and (b) blended system made of ANL-NMC and LFP in Li half cell (from Gallagher et al., [10]).

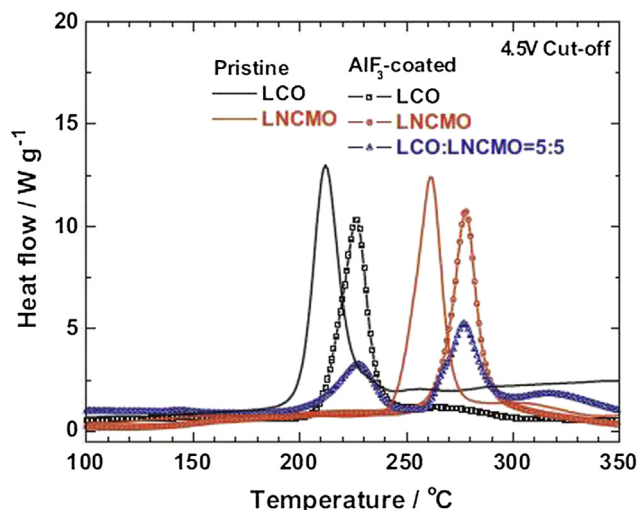


Fig. 8. Comparison of differential scanning calorimetry traces of (i) LiCoO_2 , (ii) $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, (iii) AlF_3 -coated LiCoO_2 , (iv) AlF_3 -coated $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ and (v) blended AlF_3 -coated LiCoO_2 and $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ (5:5) charged to 4.5 V (from Lee et al. [9]).

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and spinel and observed that the Li redox features due to Ni were followed by Mn redox features during the Li extraction cycle. This indicates that $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is active in the low- and high-potential regions, while, spinel exhibits activity in the intermediate region of cell voltage [44]. Blending of layered oxides with spinel helped to reduce fading of discharge capacity due to the spinel component.

2.4. Blends with $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co}$) systems

The cathode materials referred to as “ Li_2MnO_3 -stabilized” oxides, $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co}$), are unique in that they are not physical mixtures as discussed thus far, yet the Li_2MnO_3 component of the compound can be structurally distinguished [12,13]. The Li_2MnO_3 renders stability to layered structure of LiMO_2 , which in turn helps to achieve enhanced characteristics [12,13]. These cathode materials possess relatively high capacity, around $250\text{--}280\text{ mAh g}^{-1}$, but show high irreversible capacity loss in the first charge/discharge cycle. This has been attributed to the fact that Li ions extracted from the electrode during the first charge cannot be re-inserted back into layered cathode due to elimination of oxide-ion vacancies [12,13,45,46]. To address this limitation, researchers have followed a coating approach using Al_2O_3 , AlPO_4 and other ionically conductive compounds [47]. Surface coatings of ionically conductive materials counter the irreversible capacity loss to only a limited extent. An alternate approach to counter capacity loss is to apply a coating of Li insertion compounds like LiV_3O_8 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$, and VO_2 [3,48]. Kang and Thackeray [11] studied the effect of coating of $0.5(\text{Li}_2\text{MnO}_3)-0.5(\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2)$ with LiNiPO_4 and found substantially improved capacity retention during cycling (see Fig. 9) and substantially increased rate capability relative to uncoated layered oxide [11]. In addition to Li_2MnO_3 -stabilized oxides, researchers have developed $\text{Li}_4\text{Mn}_5\text{O}_{12}$ -stabilized [3], LiV_3O_8 -stabilized [3] and lithium free VO_2 -stabilized [48] oxides to achieve enhanced characteristics.

Recently Smith et al., [49] observed that the addition of NMC to LMO lead to an improvement in capacity retention that was larger than what authors had expected. Also, they showed the degradation of coulombic efficiency as manganese content in the anodes increased [49].

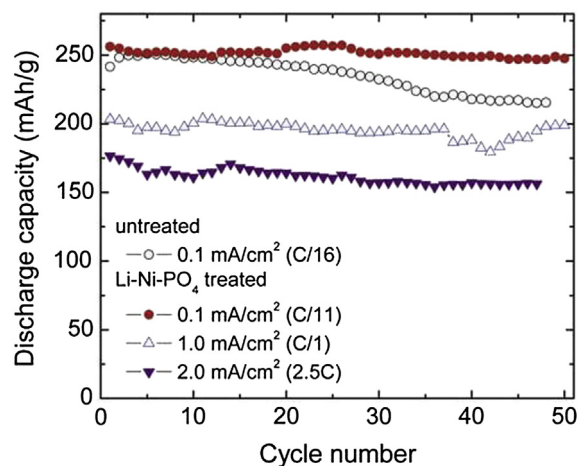


Fig. 9. Capacity vs. cycle number for lithium half cells with untreated and LiNiPO_4 -treated $0.5(\text{Li}_2\text{MnO}_3)-0.5(\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2)$ electrodes between 2.0 and 4.6 V at various discharge rates ($0.1\text{--}2.0\text{ mA cm}^{-2}$, charging current: 0.1 mA cm^{-2} for all cycles) (from Kang et al., [11]).

2.5. General trends of blended cathode systems

Generally speaking, we have noticed that blended cathode materials can exhibit a more balanced set of properties than the parent materials of which the blends are comprised. To a first approximation this is obviously due to the weighted averaging of the properties of the parent materials; however, with regards to certain properties, such as OCV and rate capability, the effects of blending are not as straightforward. Large disparities in the OCV vs. RE behavior of the parent materials, for example, can result in the low-voltage component remaining somewhat dormant with regards to Li insertion or extraction in relatively high cell SOC operating regions, which may have significant implications on the cell life. If a parent compound is particularly susceptible to deterioration at a certain state of lithiation, then the blend should be adjusted to minimize the presence of this state in the cell's SOC operating range (as discussed in Section 2.1 [6,24]). Especially at relatively high operational rates, we could expect complex interactions between the two active materials at the particle level after blending, which could also be dependent upon the synthesis method of the parent material as well as the composition of the parent material itself.

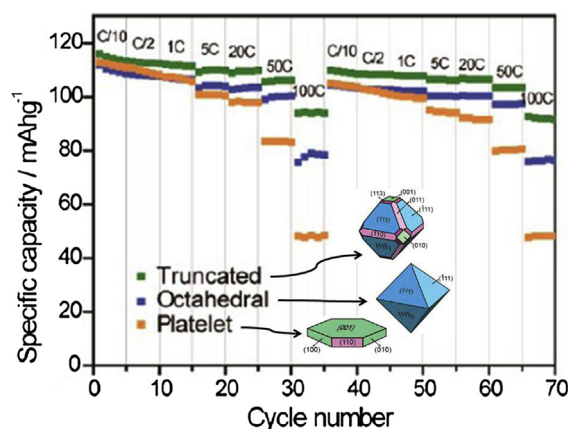


Fig. 10. Rate performance of LiMn_2O_4 electrode particles of truncated, octahedral and platelet shape during cycling at 45°C (from Kim et al. [50]).

3. Recent advances and future developments

As far as spinel is concerned, challenges still need to be addressed to achieve better cycle life. In this regard, Choi and co-workers [50] have demonstrated optimization surface structure and morphology for spinel particles in order to minimize degradation effects such as Mn dissolution. The authors demonstrated that through controlled synthesis strategy one can minimize manganese dissolution, achieve high rate capability and also retain good cycle life (see Fig. 10). In an effort to enhance rate capability, Lee et al. [51] have synthesized nano-sized (~ 20 nm) spinel particles through hydrothermal synthesis and coated them with conductive carbon. The finely sized nanoparticles possessing high surface area were then compacted into micron-sized larger aggregates. Electrodes based on such nanoparticle aggregates were shown to exhibit high energy density and high rate capability, demonstrating their possible use for high-power and fleet-vehicle electrification applications. A recent review on advances in design of high-power batteries surveys the advances in the field in the design of cathode and anode materials [52]. Besides the advances in synthesis, challenges still exist, such as large-scale manufacturing of such high-powered batteries at low cost, which in turn may accelerate faster adaptation by battery manufacturers.

Besides blending two different cathode materials, efforts are in progress to explore composite systems made of three different cathode materials. In this regard Manivannan et al. [7] have explored compositions in the ternary mixed cathode system, $(1 - x - y)\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2 \cdot x\text{Li}_2\text{MnO}_3 \cdot y\text{LiCoO}_2$ (physical mixture) which exhibits a high discharge capacity in the range 200–230 mAh g^{-1} . Among the compositions studied by authors, the Li-rich compound, $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ni}_{0.16}\text{Co}_{0.24}\text{O}_2$ exhibits high capacity of ~ 230 mAh g^{-1} . However, further studies are needed to investigate rate capability and cyclic characteristics of such ternary cathode systems. A discussion of Li-rich (i.e., over-lithiated) compounds is beyond the scope of the present review. It is generally accepted that reduced capacity during cycling can be attributed to several degradation processes which include parasitic reactions involving solvents, material degradation at the cathode and anode, binder and binder-related decay mechanisms [53–56]. These material limitations call for further improvement in the range of materials (e.g., cathode, anode, binder, solvents, salt etc) used in the design of Li ion batteries. Also, cell capacity decay follows rate laws with respect to time during storage or cycle life tests, which depend on cell chemistry [57], making it vital for optimal choices of materials for cathode designs. The search for new and improved cathode materials with high discharge capacity for hybrid and electric vehicles [58–60] remains a significant challenge. Cathode materials based on layered oxides (i.e., Li-rich compounds) hold the greatest potential for improved capacity and energy density in the near term [58,59]. Challenges for developing these materials include good cycle life and stability. Longer term, olivine fluorides ($\text{Li}_2\text{MPO}_4\text{F}$), silicates (Li_2MSiO_4) and lithium-sulfur based cathode (see Fig. 11) have significant potential but need to be developed further to meet the demands in the field of hybrid and electric vehicles [60].

4. Conclusions

This review gives an overview of emerging trends in blended cathode materials, being developed for applications in HEVs, PHEVs, and BEVs. Due to their unique combination of material characteristics, blended cathode systems can offer advantages over using a single cathode material, including reduced capacity loss, longer cycle life, reduced cost and improved thermal stability. For the blended systems with spinel, manganese dissolution remains a major shortcoming. Lithium-ion batteries employing spinel as a

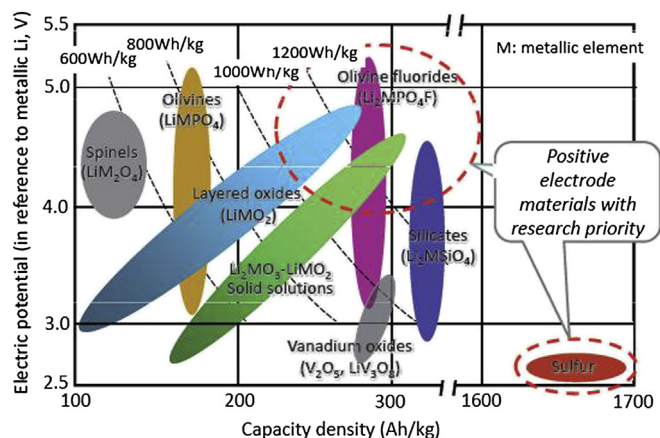


Fig. 11. Priority positive electrode materials for future research: electric potential vs. charge-capacity density (from Kawamoto, [60]). According to Kawamoto future research focus would be on cathodes marked by red circles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cathode material may therefore be particularly challenged in automotive propulsion applications where long battery life over a wide range of operating temperatures is essential. Surface modification to improve cathode particle stability and integrity and enhance cell life performance has been successfully implemented in a number of cathode systems and will likely remain a feature of either single component or blended systems. Progress in developing new approaches to improve capacity, life, and stability characteristics will continue and are likely to produce incremental improvements. Longer term, new chemistries will be needed to satisfy the energy requirements of PHEV and BEV applications. Also, fast charging is gaining momentum in order to meet the demands of the modern life style. Blended systems can be comprised of a parent cathode material which is particularly capable of high-rate charge and discharge [50]. Currently, Li-rich compounds and Li-sulfur systems hold great promise, but intermediate steps that use some of the strategies outlined here may be beneficial and the lessons learned about blending and coating cathode systems are likely to be applicable. Alternatively, advances in manufacturing will likely lead to more cost-effective existing commercial cathode materials.

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